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Atty. Docket No. KOV-012

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:	:
Christopher GUDEMAN et al.	: GROUP ART UNIT: 1752
APPLICATION NO: 10/749,876	:
FILED: DECEMBER 31, 2003	: EXAMINER: WALKE, Amanda C.
FOR: RADIATION PATTERNABLE FUNCTIONAL MATERIALS, METHODS OF THEIR USE, AND STRUCTURES FORMED THEREFROM	

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                                    By: _Jennie Heaton_
                                         Jennie Heaton

DECLARATION UNDER 37 C.F.R. 1.132

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SIR:

Now comes Joerg ROCKENBERGER, who declares and states that:

1.   I am a Chemist, currently employed by Kovio, Inc., as Manager of the Materials Development group. I have been continuously employed by Kovio, Inc. since 2001. Prior to

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2001, I was employed by the University of California, Berkeley, as a Research Associate, where my duties included research and development work in the area of nanoparticle synthesis and characterization.

2.   I received a Diploma in Chemistry from Technical University Karlsruhe, Germany, in 1995, and a Ph.D. in Physical Chemistry from University of Hamburg, Germany, in 1998.

3.   I have read the above-identified application and am familiar with the subject matter disclosed and claimed therein. I have read U.S. Pat. No. 6,921,623, to Hanabata et al. (hereinafter "Hanabata et al."). I am also familiar with nanoparticles, techniques for making and using the same, ligands for nanoparticles (including those having a photoreactive group or a group that is reactive with a photochemically generated species), techniques for forming conductive and semiconductive films from nanoparticles, radiation-based patterning techniques, and materials for semiconductor and/or electronic devices.

4.   I understand that the independent claim of the above-identified application is directed to a radiation patternable functional material, comprising:

    a)   nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals; and

    b)   a plurality of ligands bound to each of said nanoparticles, said ligands containing a photoreactive group or a group that is reactive with a photochemically generated species and that, after first-order photoreaction or reacting with said photochemically generated species, materially changes the solubility characteristics of said material in a developer,

wherein, after irradiation, developing and curing, the functional material forms a patterned film of an electronically conducting or semiconducting material.

5.   Hanabata et al. neither discloses nor suggests a radiation patternable functional material that forms a patterned film of an electronically conducting or semiconducting material.

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6.   Furthermore, Hanabata et al. do not enable one to make a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals.

7.   Hanabata et al. discloses a photosensitive resin composition comprising an active component selected from an active metal alkoxide represented by the formula (1) or a polycondensate thereof and a particle represented by the formula (2):

$$(X)_{m-n}\text{-}M^m\text{-}[(U_1)_p\text{—}(U_2\text{-}Z)_t]_n \qquad\qquad (1)$$

$$P\text{—}[(Y)_s\text{—}\{(U_1)_p\text{—}(U_2\text{-}Z)_t\}]_k \qquad\qquad (2)$$

wherein X is a hydrogen, a halogen, an alkoxy group or an alkoxycarbonyl group, M is a metal atom whose valence m is not less than 2, U_1 is a first connecting unit, U_2 is a second connecting unit and Z is a group causing a difference in solubility by light exposure, P is a fine particle carrier, Y is a coupling residue, n is an integer of not less than 1, m > n, p is 0 or 1, t is 1 or 2, k is an integer of not less than 1, and s is 0 or 1 (Abstract, ll. 1-16).

8.   The composition of Hanabata et al. is intended as a high-resolution photoresist material, not as an electronically conducting or semiconducting material.

9.   For example, at col. 3, ll. 13-32, Hanabata et al. disclose that the combination of an active component and a photosensitive resin composition can form a high resolution pattern with high sensitivity when a functional group is introduced into the active component. Hanabata et al. further teach that a fine or finely divided particle (an active particle) can become hydrophilic by eliminating a hydrophobic leaving group upon light exposure, and the active component can be a specific metal alkoxide (an active metal alkoxide) or the polycondensate thereof (an active particle formed by polycondensation). Thus, according to Hanabata et al., light exposure can cause a difference in solubility, and the combination of the metal alkoxide or a polycondensate thereof, and a photosensitive resin composition, may form a high(er) resolution pattern with higher sensitivity because of a reduction of impurity incorporation. This disclosure

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of Hanabata et al. strongly suggests application of the composition disclosed therein as a photoresist.

10.   The invention of Hanabata et al. includes a photosensitive resin composition which comprises a base resin, a photosensitizer and the active component (col. 5, ll. 45-48). To form a pattern, the photosensitive composition may be applied or coated onto a substrate, the coating layer may be exposed to light, the light-exposed layer may be heat-treated, and the heat-treated layer may be developed (col. 5, ll. 54-58 of Hanabata et al.).

11.   The active component (or ingredient) in the invention of Hanabata et al. is used (or usable) in combination with a photosensitizer which constitutes a photosensitive resin composition, and has a unit for causing a difference in solubility owing to at least light exposure (col. 6, ll. 27-31). The active component comprises at least one member selected from the group consisting of the active metal alkoxide represented by the formula (1) above or the polycondensate thereof, and the particle represented by the formula (2) above (col. 6, ll. 31-35 of Hanabata et al.).

· 12.   Although many possible metals are contemplated, Hanabata et al. teach that the metal atom M may be aluminum, titanium, zirconium or silicon, and is usually silicon (col. 4, ll. 33-34; emphasis added). This list of metals for metal atom M is consistent with the teachings of Hanabata et al. relating to the prior photoresist approach(es) discussed at col. 1, ll. 21-47 and col. 2, ll. 5-7. Thus, the photosensitive composition Hanabata et al. forms a patternable *resist* material, rather than a patterned electronically conducting or semiconducting material.

13.   Therefore, Hanabata et al. does not disclose a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, having ligands bound thereto that can change the solubility characteristics of the material in a developer and *that forms a patterned film of an electronically conducting or semiconducting material* (see the description of the present invention in paragraph 4 above).

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14.   Furthermore, when their composition contains a particle or polycondensate, Hanabata et al. do not enable one to make a patternable material comprising semiconductor and/or metal nanoparticles having ligands bound thereto that can change the solubility characteristics of the material in a developer and that, after irradiation, developing and curing, can form a patterned film of an electronically conducting or semiconducting material.

15.   Regarding the polycondensate, the polycondensate of Hanabata et al. may be a polycondensate of the active metal alkoxide represented by the formula (1) alone (singly) or a polycondensate (copolycondensate) of the active metal alkoxide represented by the formula (1) and a metal alkoxide represented by the following formula (5):

$$(X)_{m-n-1}M^m(R^5)_{n-1} \qquad\qquad (5)$$

wherein R^5 represents a hydrogen atom or an alkyl group, and X, M, m and n have the same meanings as described in paragraph 7 above (col. 4, l. 65-col. 5, l. 8 of Hanabata et al.), although it is not clear how the compound of formula (5) can be a metal alkoxide when X is hydrogen, a halogen, or an alkoxycarbonyl group. In one embodiment, the polycondensate of Hanabata et al. is an active particle formed by polycondensation (col. 3, ll. 23-26).

16.   Consistent with the disclosure described in paragraph 15 above, Hanabata et al. teach that an active component (especially an active particle) may comprise a polycondensate of the above-mentioned active metal alkoxide. Such an active component may be an active particle in the form of a particulate (particulate matter), or a liquid or solid oligomer. The active component [or, presumably] the polycondensate of the active component can be obtained by polycondensing the active metal alkoxide by a conventional sol-gel method to form of a polymer or a sol (col. 14, ll. 44-53).

17.   As is known in the art, polycondensation (or polymerization) of metal alkoxides by the sol-gel method leads to formation of metal oxides, and not the corresponding metal. Therefore, any material, compound or composition based on the polycondensate of Hanabata et al. does not and cannot form a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing.

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18.   Regarding the particles, Hanabata et al. teach that the particle P (see formula (2) in paragraph 7 above) may be an organic fine particle carrier or an inorganic fine particle carrier (e.g., silicasol; see, e.g., col. 3, ll. 51-56; col. 5, ll. 17-19; and col. 17, l. 51-col. 18, l. 14). However, the organic fine particle carriers listed by Hanabata et al. at col. 17, ll. 51-61 (styrenic resins, [meth]acrylic resins, a silicone resin, thermosetting resins such as polyamide resins, a crosslinked melamine resin and a crosslinked guanamine resin) do not and cannot form a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing.

19.   In the passage at col. 18, ll. 1-14, Hanabata et al. disclose a number of inorganic fine particle carriers, including a metal alone (simple or single metal; e.g., gold, silver, copper, platinum, aluminum), an inorganic oxide (e.g., silica [e.g., silica sol such as colloidal silica, aerogels, glass], alumina, titania, zirconia, zinc oxide, copper oxide, lead oxide, yttrium oxide, tin oxide, indium oxide, magnesium oxide), an inorganic carbonate (e.g., calcium carbonate and magnesium carbonate), an inorganic sulfate (e.g., barium sulfate and calcium sulfate), a phosphate (e.g., calcium phosphate and magnesium phosphate), and the like, which include sols and gels prepared by, for example, a sol-gel method, and which can be used either singly or in combination. Thus, out of the five generic inorganic fine particle carrier types (not including the sols and gels), all but one are clearly expected to form an electrical insulator after functionalization (i.e., formation of the compound of formula (2) from the particle), irradiation, developing and curing.

20.   In the one remaining example of a particle (a metal alone), Hanabata et al. do not enable one to form a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing of a composition including a compound having a metal particle. This is because Hanabata et al. discloses and enables formation of an insulator film or a somewhat random distribution of particles (which may or may not have properties of a metal) embedded in an insulator matrix, rather than a patterned film of an electronically conducting or semiconducting material.

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21.   For example, to form the particles of formula (2) above, Hanabata et al. enable use of only particles (be they organic or inorganic) having hydroxide (or a combination of hydroxide and oxide) groups on the surface for linking to a coupling agent residue Y. Hanabata et al. teach that a hydrophilic group is introduced into an inorganic fine particle through both a coupling agent and a connecting unit (col. 16, ll. 63-65). Each component may be bonded by reacting a connecting unit U having two hydroxyl groups with a coupling agent Y having an isocyanate group (e.g., a silane coupling agent) to form a compound having a free hydroxyl group and a coupling group (an alkoxy group or a halogen atom), wherein the coupling agent is bonded to one of hydroxyl groups of the unit; protecting the free hydroxyl group by a protective group such as t-BOC group; and then reacting an inorganic fine particle carrier (e.g., silicasol, etc.) with the coupling group (the alkoxy group or the halogen atom; see col. 16, l. 65-col. 17, l. 9). Other processes may be employed, but they also appear to bind the hydrophilic group-containing compound with the particle via the alkoxy group or halogen atom site in the coupling agent (see, e.g., col. 17, ll. 10-30 of Hanabata et al.). Thus, Hanabata et al. teach that an alkoxy group or halogen atom in the coupling agent is required for introducing the hydrophilic group (i.e., the group giving the composition its photosensitive properties; see, e.g., col. 3, l. 66-col. 4, l. 17) into a fine particle (be it an inorganic particle or another type of particle).

22.   Specifically with regard to the inorganic particle, Hanabata et al. disclose examples of coupling agents (corresponding to a residue Y in formula (2) above) including an organic metal compound containing an alkaline earth metal, a transition metal, a rare earth metal, or a metal element of the Groups 3 to 5 and 13 to 15 of the Periodic Table of Elements, especially a metal element of the Groups 4, 13 and 14 of the Periodic Table of Elements, for example, aluminum, titanium, zirconium, and silicon. Among the organic metal compounds, a titanium coupling agent and a silane coupling agent (especially the silane coupling agent) are preferred (col. 18, l. 41-51).

23.   The silane coupling agent includes the coupling agents represented by the formula (4):

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$$(R^6)_w Si(D)_{4-w} \qquad\qquad\qquad (4)$$

24.   The reactive group D corresponding to the fine particle carrier of the coupling agent (4) is usually a halogen atom (bromine atom, chlorine atom, etc.), or a hydrolytic condensable group such as an alkoxy group (e.g., a C_{1-4} alkoxy group such as methoxy group and ethoxy group; see col. 18, ll. 52-59 of Hanabata et al.). As is known in the art, many metal halides such as $TiCl_4$ and $SiCl_4$ are reactive towards oxygen-containing compounds (see, e.g., Cotton et al., "Advanced Inorganic Chemistry," John Wiley & Sons, New York (1999), pp. 271-272, 283-285, 472-474, and 558-559, attached hereto), and the hydrolytic condensable groups of Hanabata et al. result in the formation of metal-oxygen-silicon bonds, typically from a hydroxy group on the metal. Thus, the silane coupling agents disclosed by Hanabata et al. are known to be reactive with the oxygen-containing species, such as oxo or hydroxy groups (which are bound directly to a metal; i.e., metal oxides and/or hydroxides).

25.   On the other hand, the silane coupling agents disclosed by Hanabata et al. are not expected to react with metal or semiconductor particles not having oxygen-containing species on the surface (at least not in any manner that would result in formation of a compound of the formula (2) as described in paragraph 7 above).

26.   For example, of the five (5) metals disclosed by Hanabata et al. at col. 18, ll. 1-3, three (3) are generally considered not to form significant amounts of oxide on corresponding particle surfaces (i.e., gold, silver and platinum). Based on the disclosures discussed in this Declaration, Hanabata et al. do not enable coupling of a coupling agent to metal particles that do not form oxide surfaces. Instead, and as an example of why such a coupling reaction as taught by Hanabata et al. would fail, an attempt to couple the silane coupling agent to such metal particles under state of the art coupling conditions would be likely to crosslink the silane coupling agent, rather than couple it to the metal nanoparticle. Thus, if the "metal alone" particle of Hanabata et al. is capable of coupling with the silane coupling agent in the manner disclosed therein, the "metal alone" particle of Hanabata et al. must be one that contains a sufficiently large number of hydroxide and/or oxide groups on its surface to enable the coupling reaction to occur

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to an extent enabling isolation of the coupling reaction product. However, the silane cross-linking reaction consumes twice as much coupling agent as the coupling reaction, and is reasonably expected to have a faster reaction rate than the coupling reaction, so one would not expect a reaction between particles of gold, silver or platinum alone and the silane coupling agent of formula (4) above to result in an amount of coupling reaction product that can be reasonably isolated. As a result, and consistent with the remainder of their disclosure, Hanabata et al. does not enable formation of particles of the formula (2), where P is a particle of gold, silver or platinum alone.

27.   The remaining metals disclosed by Hanabata et al. at col. 18, ll. 1-3 (copper and aluminum) readily form oxide surfaces (e.g., on exposure to air, oxygen or other oxygen-containing oxidant such as hydrogen peroxide). As a result, copper or aluminum metal particles as disclosed by Hanabata et al. would be expected to have a sufficiently large number of oxide and/or hydroxide groups on their surfaces to couple to the silane coupling agent in the manner disclosed and taught by Hanabata et al. and provide an amount of coupling reaction product that can be reasonably isolated. Such a large number of oxide and/or hydroxide groups on the surface of a copper or aluminum particle would effectively prevent formation of patterned film of an electronically conducting or semiconducting material, after irradiation, developing and curing, particularly after functionalization with the coupling agents, U_1/U_2 connecting units and light-sensitive Z functional groups (see formula (2) above and the discussion of cross-linking vs. coupling reactions in paragraph 27 above).

28.   Once functionalized in the manner taught by Hanabata et al., the composition of Hanabata et al. forms an insulator film or a distribution of particles embedded in an insulator matrix, rather than a patterned film of an electronically conducting or semiconducting material. For example, the active (or photoactive) component of Hanabata et al. (i.e., the active metal alkoxide, its polycondensate, and/or an active particle represented by the formulas (1) and (2)) is advantageously used (usable) *in combination with a photosensitive resin composition* (col. 20, ll. 60-67; emphasis added). The photosensitive resin (or resist) composition of Hanabata et al. may comprise a photosensitizer and the above-mentioned active component, but usually it

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comprises a base resin (an oligomer or a polymer), a photosensitizer and the above-mentioned active component (col. 21, ll. 50-55). Of the resins listed from col. 21, l. 56 through col. 25, l. 43, none are known to result in formation of a patterned film of an electronically conducting or semiconducting material. Instead, these resins are generally known to form an insulator film (or in the case where particles are present, a distribution of particles embedded in an insulator matrix) after irradiation, developing and curing.

29.   For example, Hanabata et al. teach that the amount of the active component in their photosensitive resin composition can be from about 0.01 to 1000 parts by weight, on a solid matter basis, relative to 100 parts by weight of the base resin. The amount of active component is usually from about 5 to 1000 parts by weight, preferably about 10 to 500 parts by weight and more preferably about 10 to 300 parts by weight, especially about 10 to 100 parts by weight, relative to 100 parts by weight of the base resin on a solid matter basis. (Col. 27, ll. 14-23 of Hanabata et al.) As a result, when the photosensitive resin composition of Hanabata et al. further includes a base resin, the photosensitive resin composition of Hanabata et al. forms an insulator film or (in the case where particles are present) a distribution of particles embedded in an insulator matrix, after irradiation, developing and curing.

30.   The photosensitive resin composition of Hanabata et al. can be prepared in accordance with a conventional method, for example, by mixing a photosensitive resin [a base resin and a photosensitizer] and an active component. The photosensitive resin composition usually contains a solvent (e.g., the solvents exemplified in the section of the active metal alkoxide). (Col. 27, ll. 33-45 of Hanabata et al.)

31.   The photosensitive layer of Hanabata et al. can be formed by applying (spreading or coating) the above-described photosensitive resin composition to a substrate (a base material; see col. 27, ll. 47-49 of Hanabata et al.), and patterns can be carried out by a conventional lithography technique (i.e., a combination of exposure, development and etching; see col. 28, ll. 52-54 of Hanabata et al.). Hanabata et al. also teach that their coated film may be subjected to heat- or cure-treatment at a suitable temperature in an appropriate step from application of the photosensitive resin composition to development. If necessary, for example, after development,

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the coated film of Hanabata et al. may be subjected to heat-treatment (col. 29, ll. 61-67 of Hanabata et al.), but no particular temperature, temperature range or temperature effective to provide a desired result is disclosed. Thus, when the photosensitive resin composition of Hanabata et al. includes a base resin, it is expected to form an insulator film or (in the case where particles are present) a distribution of particles embedded in an insulator matrix, after irradiation, developing and curing.

32.   However, even if the active component (i.e., compound[s] of the formulas (1) and (2) above) is used without a base resin as the photosensitive resin composition (although Hanabata et al. does not disclose any examples of such a composition), those particles P disclosed by Hanabata et al. that are capable of coupling to the coupling agent in a manner enabling reasonable isolation of a compound of the formula (2) would be expected to form a distribution of particles embedded in an insulator matrix, after irradiation, developing and curing. The particles of formula (2) capable of being made in an amount that can be reasonably isolated would not be capable of forming a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing.

33.   Consequently, all of the particles (organic, inorganic or metal) disclosed by Hanabata et al. form oxides or other electrical insulators after functionalization with the coupling agent, irradiation, developing and curing. Hanabata et al. disclose no reaction, technique or special set of conditions under which their silane coupling agent(s) are capable of forming a particle having photosensitive ligands bound thereto that is capable of forms a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing.

34.   As an alternative to the silane coupling agent, the organic metal compounds of Hanabata et al. containing, as the metal M, aluminum, titanium or zirconium, may be exemplified by the organic metal compounds corresponding to the silane coupling agents (col. 19, ll. 3-7). Thus, the possibility of metals other than silicon in the coupling agent of Hanabata et al. does not enable formation of a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, and a plurality of ligands bound to each of the nanoparticles, that

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forms a patterned film of an electronically conducting or semiconducting material after irradiation, developing and curing.

35.   Therefore, Hanabata et al. does not enable one skilled in the art to make a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, having ligands bound thereto that can change the solubility characteristics of the material in a developer and that forms a patterned film of an electronically conducting or semiconducting material (see the description of the invention in paragraph 4 above).

36.   Furthermore, Hanabata et al. further teach the importance of a transparent particle. For example, when the mean particle size of the active particle is smaller than an exposing wavelength, because the active particle is substantially transparent to the exposing wavelength, light exposure can be conducted to the depth of the photosensitive layer even if the layer is thickened (col. 15, ll. 56-60). As a result, sensitivity and resolution can be improved as much as a pattern with high sensitivity and high resolution can be formed in regard to a light source of shorter wavelength (col. 15, ll. 60-63). These disclosures by Hanabata et al. further emphasize the application of the compounds of formulas (1) and (2) above to photolithography and photoresist compositions.

37.   The use of UV-absorbent metal nanoparticles may be detrimental to the suggested advantages of the invention of Hanabata et al. While it is generally understood in the art that nanoparticles having a size less than 100 nm do not scatter light (assuming they are not agglomerated in larger secondary particles), many metal nanoparticles (in particular gold, silver, and copper) have one or more strong characteristic UV absorptions. These absorptions would be expected to reduce the sensitivity of the resist of Hanabata et al., and limit its usefulness for high resolution patterning.

38.   Further, Declarant sayeth not.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these

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statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issued thereon or therefrom.

Joerg ROCKENBERGER   05/22/2006
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Fluorides

These are obtained by fluorination of the other halides or by direct interaction; GeF_4 is best made by heating $BaGeF_6$. Tetrafluorides of Si and Ge are hydrolyzed by an excess of water to the hydrous oxides; the main product from SiF_4 and H_2O in the gas phase is $F_3SiOSiF_3$. In an excess of aqueous HF, the hexafluoro anions (MF_6^{2-}) are formed. These anions are also found with certain trivalent cations, e.g., $SmSnF_7$ and $TlPbF_7$.[31] Similarly, a solid state reaction of tin metal and $(NH_4)HF_2$ gives:

$$2Sn + 7(NH_4)HF_2 \xrightarrow{\;300°C\;} 2(NH_4)_3SnF_7 + 4H_2 + NH_3$$
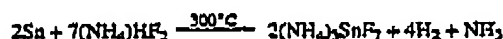
In these EF_7^- species the stiochiometry might be misleading in regard to their structure because they all contain $[SnF_6]^{2-}$ octahedra and F^- anions surrounded by the corresponding cations.[32] Germanium tetrafluoride can be reduced to give hygroscopic mixed-valent species such as Ge_5F_{12} and Ge_7F_{16}.[33] Tin tetrafluoride is polymeric, with Sn octahedrally coordinated by four bridging and two nonbridging F atoms. Non-stoichiometric lead tetrafluoride is made by the action of F_2 on PbF_2, but the pure material can be prepared by high-pressure fluorination of "PbF_{4-x}"; it is isostructural with SnF_4.[34]

Silicon Halides

Silicon tetrachloride is made by chlorination of Si at red heat. Hexachlorodisilane (Si_2Cl_6) can be obtained by interaction of $SiCl_4$ and Si at high temperatures or, along with $SiCl_4$ and higher chlorides, by chlorination of a silicide such as that of calcium. The higher members, which have highly branched structures, can also be obtained by amine-catalyzed reactions such as

$$5Si_2Cl_6 \longrightarrow Si_6Cl_{14} + 4SiCl_4$$

$$3Si_3Cl_8 \longrightarrow Si_5Cl_{12} + 2Si_2Cl_6$$
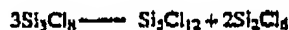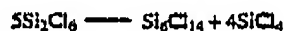
and by photolysis of $SiHCl_3$. The products are separated by fractional distillation.

All the chlorides are immediately and completely hydrolyzed by water, but careful hydrolysis of $SiCl_4$ gives $Cl_3SiOSiCl_3$ and $(Cl_3SiO)_2SiCl_2$.

Hexachlorodisilane is a useful reducing agent for compounds with oxygen bound to S, N, or P; under mild conditions, at 25°C in $CHCl_3$ chlorooxosilanes are produced. It is particularly useful for converting optically active phosphine oxides $R^1R^2R^3PO$ into the corresponding phosphine. Since the reduction is accompanied by configurational inversion, the intermediacy of a highly nucleophilic $SiCl_3^-$ ion (*cf.* PCl_3) has

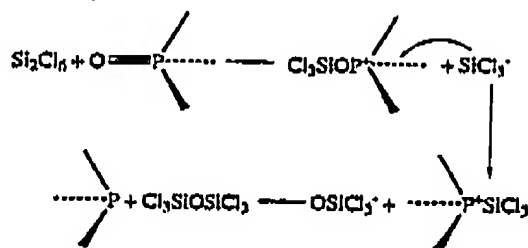[31]O. Graudejus and B. G. Müller, *Z. anorg. allg. Chem.* 1996, 622, 1601.
[32]C. Plitzko and G. Meyer, *Z. anorg. allg. Chem.* 1997, 623, 1347.
[33]J. Köhler and J.-H. Chang, *Z. anorg. allg. Chem.* 1997, 623, 596.
[34]M. Bork and R. Hoppe, *Z. anorg. allg. Chem.* 1996, 622, 1557.

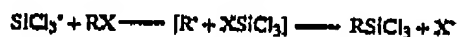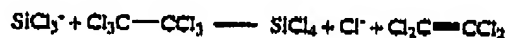**272** *chapter 8/*THE GROUP 14 ELEMENTS: Si, Ge, Sn, Pb

been proposed:

The postulation of $SiCl_3^-$ can also accommodate the equally useful, clean, selective reductions by trichlorosilane (bp 33°C) and also the formation of C—C and Si—C bonds by reaction of $SiHCl_3$ with CCl_4, RX, RCOCl, and other halogen compounds in the presence of amines. In these cases the hypothetical $SiCl_3^-$ could be generated by the reaction
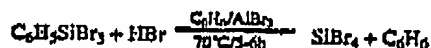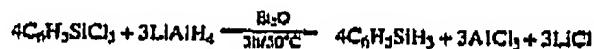
$$HSiCl_3 + R_3N \rightleftharpoons R_3NH^+ + SiCl_3^-$$

followed by

$$SiCl_3^- + Cl_3C—CCl_3 \longrightarrow SiCl_4 + Cl^- + Cl_2C=CCl_2$$

$$SiCl_3^- + RX \longrightarrow [R^- + XSiCl_3] \longrightarrow RSiCl_3 + X^-$$

There is precedent for the postulation of the $SiCl_3^-$ ion, since trisubstituted organosilanes (R_3SiH), react with bases to give silyl ions (R_3Si^-).

Silicon tetrabromide[33] can be prepared by a multi-step procedure by reaction of $C_6H_5SiCl_3$ with $LiAlH_4$ then Br_2 and finally HBr according to:

$$4C_6H_5SiCl_3 + 3LiAlH_4 \xrightarrow[\text{3h/30°C}]{\text{Et}_2\text{O}} 4C_6H_5SiH_3 + 3AlCl_3 + 3LiCl$$

$$C_6H_5SiH_3 + 3Br_2 \xrightarrow[\text{0°C to 80°C}]{\text{CCl}_4/\text{N}_2} C_6H_5SiBr_3 + 3HBr$$

$$C_6H_5SiBr_3 + HBr \xrightarrow[\text{70°C/3-4h}]{\text{C}_6\text{H}_6/\text{AlBr}_3} SiBr_4 + C_6H_6$$

It can also be prepared from the elements. The fuming liquid is decomposed by water into silicic acid and HBr with great evolution of heat; it reacts violently with potassium.

Chloride Oxides

A variety of chlorooxosilanes, both linear and cyclic, is known. Thus controlled hydrolysis of $SiCl_4$ with moist ether, or interaction of Cl_2 and O_2 on hot silicon, gives $Cl_3SiO(SiOCl_2)_nSiCl_3$, where $n = 1$ to 4.

[33]H.-G. Horn and D. Kuczkowiak, *Z. anorg. allg. Chem.* **1996**, *622*, 1083.

The three germanium atoms form an equilateral triangle similar to that of the carbon analogue, the cyclopropenium ion;[67] the cation has Ge—Ge bonds (Section 8-12).

Neutral Species[68]

These are numerous and quite varied in type. Some are 4-coordinate such as SnX_4 and $X_nSn(NR_2)_{4-n}$,[69] but the majority are 6-coordinate, examples being trans-$SnCl_2$ (β-dike)$_2$, $SnCl_2(S_2CNEt_2)_2$, $Sn[(OC_2H_4)_2N(C_2H_4OH)]_2$, and porph SnX_2.[70] Both lower and higher coordination numbers also occur, examples being five in PbSi(o-$C_6H_4O_2$)$_2$ and presumably seven or eight in $Sn(S_2CNEt_2)_4$.

Adducts

The tetrahalides are prone to add neutral ligands to form adducts that are usually 6-coordinate. Typical examples are trans-SiF_4(py)$_2$, cis-SiF_4(bipy), $SiCl_4L_2$ (L = py, PMe$_3$), and numerous cis-SnX_4(L—L) and cis or trans-SnX_4L_2 compounds.

The Lewis acid order is $SnCl_4 > SnBr_4 > SnI_4$.

8-10 Alkoxides, Carboxylates, and Oxo Salts

All four elements form alkoxides, but those of silicon, for example, $Si(OC_2H_5)_4$, often called silicate esters, are the most important; the surface of glass or silica can also be alkoxylated. They can be used in the synthesis of ceramic materials.[71] Alkoxides are normally obtained by the standard method:

$$MCl_4 + 4ROH + 4 \text{ amine} \longrightarrow M(OR)_4 + 4 \text{ amine·HCl}$$

Silicon alkoxides are rapidly hydrolyzed by water, eventually to hydrous silica, but polymeric hydroxo alkoxo intermediates occur. Organo alkoxides such as the silyl ester (MeO)$_3$SiMe and its derivatives are widely known.[72]

Of the carboxylates, lead tetraacetate is the most important because it is used in organic chemistry as a strong but selective oxidizing agent.[73] It is made by dissolving Pb$_3$O$_4$ in hot glacial acetic acid or by electrolytic oxidation of Pb^{II} in acetic acid. In oxidations the attacking species is generally considered to be Pb(O$_2$CMe)$_3^+$, which is isoelectronic with the similar oxidant Tl(O$_2$CMe)$_3$, but this is not always so, and some oxidations are known to be free radical in nature. The trifluoroacetate is a white solid, which will oxidize even heptane to give the CF$_3$CO$_2$R species, from which the alcohol ROH is obtained by hydrolysis; benzene similarly gives phenol.

The tetraacetates of Si, Ge, Sn, and Pb also form complex anions such as [Pb(O$_2$CMe)$_6$]$^{2-}$ or [Sn(O$_2$CMe)$_3$]$^-$. For M(O$_2$CMe)$_4$, Si and Ge are 4-coordinate

[67]A. Sekiguchi et al., Science 1997, 275, 60.
[68]C. Y. Wong and J. D. Woollins, Coord. Chem. Rev. 1994, 130, 175.
[69]See for example: H. Schmidbaur et al., Chem. Ber./Recueil 1997, 130, 1159; 1167.
[70]D. P. Arnold and J. P. Bartley, Inorg. Chem. 1994, 33, 1486.
[71]T. J. Boyle and R. W. Schwartz, Comments Inorg. Chem. 1994, 16, 243.
[72]J. G. Verkade et al., Inorg. Chem. 1990, 29, 1065.
[73]T. L. Holton and H. Shechter, J. Org. Chem. 1995, 60, 4725.

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with unidentate acetate; Pb has only bidentate acetates, whereas the smaller Sn has a very distorted dodecahedron.

Tin(IV) sulfate, $Sn(SO_4)_2\cdot 2H_2O$, can be crystallized from solutions obtained by oxidation of Sn^{II} sulfate; it is extensively hydrolyzed in water.

Tin(IV) nitrate is obtained as a colorless volatile solid by interaction of N_2O_5 and $SnCl_4$; it contains bidentate NO_3^- groups giving dodecahedral coordination. The compound reacts with organic matter.

8-11 Organo Compounds

The general formula is $R_{4-n}EX_n (n = 0$ to 3), where R is alkyl or aryl and X is any of a wide variety of atoms or groups (H, halogen, OR', NR_2', SR', $Mn(CO)_5$, etc.). The elements may also form part of heterocyclic rings or cages,[14] for example $(R_2EO)_3$ or the silsesquioxanes $[RSiO_{3/2}]_n$,[15] such as $R_8Si_8O_{12}$ (8-IX).

(8-IX)
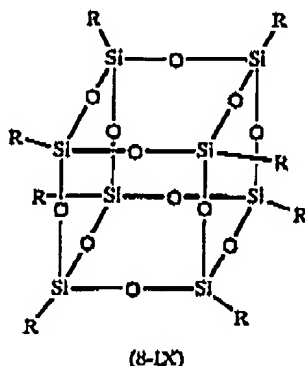
For a given class of compounds, members with C—Si and C—Ge bonds have higher thermal stability and lower reactivity than those with bonds to Sn and Pb. In catenated compounds similarly, Si—Si and Ge—Ge bonds are more stable and less reactive than Sn—Sn and Pb—Pb bonds; for example, Si_2Me_6 is very stable, but Pb_2Me_6 blackens in air and decomposes rapidly in CCl_4, although it is fairly stable in benzene.

The bonds to carbon are usually made *via* interaction of lithium, mercury, or aluminum alkyls or RMgX and the Group 14 halide, but there are many special synthetic methods, some of which are noted later.

Silicon and Germanium

The organo compounds of Si and Ge are very similar in their properties. We discuss only Si compounds.

[14]See for example: P. G. Harrison, *J. Organometal. Chem.* 1997, 542, 141 (a review on silicate cages, 221 references).
[15]F. J. Feher *et al.*, *Chem. Commun.* 1997, 1185.

Silicon-carbon bond dissociation energies are less than those of C—C bonds but are still quite high, in the region 250 to 335 kJ mol^{-1}. The tetraalkyls and -aryls are hence thermally quite stable; $Si(C_6H_5)_4$, for example, boils unchanged at 530°C.

The chemical reactivity of Si—C bonds is generally greater than that of C—C bonds because (a) the greater polarity of the bond $Si^{\delta+}—C^{\delta-}$ allows easier nucleophilic attack on Si and electrophilic attack on C than for C—C compounds, and (b) displacement reactions at silicon are facilitated by its ability to expand the coordination number above 4 by utilization of d orbitals.

The reactions of Si compounds have no mechanism analogous to S_N1 reactions at carbon and are generally complicated. Substitution reactions at 4-coordinate silicon characteristically proceed via an associative mechanism involving 5-coordinate transition states. Retention or inversion of stereochemistry may occur depending on the nature of the entering or leaving groups, namely,
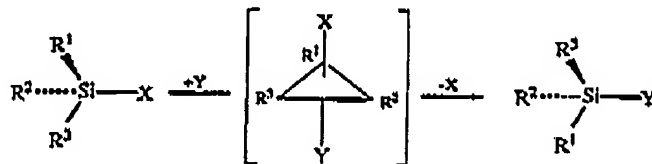
With the same leaving group, both retention and inversion can be observed; hard nucleophiles tend to attack equatorially to give retention, soft ones apically leading to inversion. Mechanisms depend crucially on the solvent used. If this has donor ability like DMF or DMSO it may attack first to form the 5-coordinate species and is then displaced by an incoming nucleophile.

A characteristic feature of organosilicon (and -germanium) chemistry, setting it strikingly apart from carbon chemistry, is the great ease with which R_3Si (and R_3Ge) groups migrate; a factor of up to 10^{12} as compared to analogous carbon compounds is typical. Among the best studied migration reactions are anionic 1,2-shifts, represented generally by the equation:
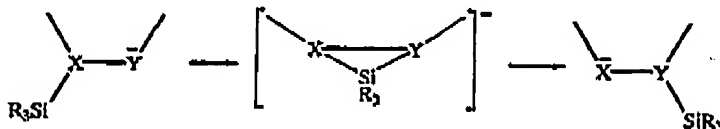
where X—Y may be N—N, O—N, or S—C. As indicated, a transition state involving 5-coordinate Si is postulated; since carbon has no valence shell d orbitals, it cannot form such a transition state easily, and such 1,2-shifts are "forbidden" in the Woodward-Hoffmann sense.

Radicals are less important in silicon than in carbon chemistry. However, silicon radicals have been detected in solution by esr and have been isolated in matrices. They are made by hydrogen abstraction with t-butoxy and other radicals generated photochemically, for example,

$$R_3SiH + Me_3CO^{\bullet} \longrightarrow R_3Si^{\bullet} + Me_3COH$$

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11-11 Alkoxides and Aryloxides

In solution in alcohols, particularly methanol, metal ions may be solvated just as in water, but the solvent molecules are usually readily displaced by stronger donor ligands such as water itself.

Just as coordinated water can lose a proton (to give hydroxo complexes), so can alcohols:

$$M-O\diagdown^{R}_{H} \rightleftharpoons [MOR]^{-} + H^{+}$$
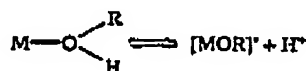
Alkoxide ligands,[52] RO⁻, and related oxygen donor ligands such as aryloxides and trialkyl- or triarylsiloxides are hard σ-donors and may also act as π-donors as a result of their filled oxygen $p\pi$-orbitals. They may therefore stabilize metal atoms in relatively high (unusually high) oxidation states, e.g., $Mo(OMe)_6$, and by the selection of appropriate steric properties, they may stabilize metal ions in unusual coordination environments as in $Cr(OBu^t)_4$. As ancillary ligands, the RO σ/π-donation may be adjusted by selection of R. The degree of π-donation is responsive to substrate uptake and release in an analogous manner to say, the slippage of indenyl ligands (η^5—η^3—η^1) or the bending of the M—N—O angle of a nitrosyl ligand.

Although M—OR groups are usually bent, in $[ZrCl_4(OMe)(MeOH)]^-$, the ZrOC angle is 171.4°, compatible with a triple bond Zr≡O—Me.

Alkoxides are known for practically every element of the s, p, d,[53] and f[54] blocks of the Periodic Table and form many heterometallic complexes.[55] They are usually made by reaction of metal halides and alcohols (or phenols) in the presence of a HX acceptor, for example,

$$TiCl_4 + 4EtOH + 4Et_3N \longrightarrow Ti(OEt)_4 + 4Et_3NH^+Cl^-$$
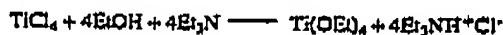
or by use of alkali metal or Tl^I alkoxides. They are normally readily hydrolyzed but thermally stable, distillable liquids or volatile solids. These properties have been used for the preparation of sol-gels for the production of ceramic materials[56] and high purity oxides of the refractory metals by pyrolysis of metal alkoxides. They undergo a wide variety of other reactions such as insertions with small molecules, for example,

$$L_nMOR + CO_2 \longrightarrow L_nM\diamond^{O}_{O}COR$$
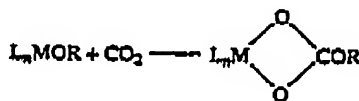
[52]M. H. Chisholm, *Chem. Soc. Rev.* 1995, 79.
[53]W. A. Herrmann *et al*, *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 2187.
[54]W. G. Van Der Sluys and A. P. Sattelberger, *Chem. Rev.* 1990, *90*, 1027.
[55]K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.* 1990, *90*, 969.
[56]R. C. Mehrotra and A. Singh, *Chem. Soc. Rev.* 1996, 1.
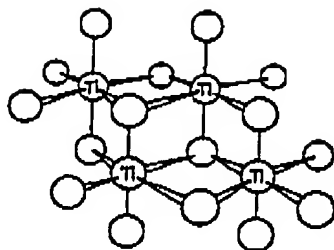
Figure 11-3 The tetranuclear structure of crystalline [Ti(OC₂H₅)₄]₄ showing both μ_2 and μ_3 bridges. Only Ti and O atoms are shown. Note that the more bulky trifluoromethyl compound is mononuclear.

and hydrogenolysis, for example,

$$(CuOBu^t)_4 \xrightarrow[PR_3]{H_2} (HCuPR_3)_6 + Bu^tOH$$
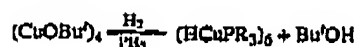
Nitriles, such as CH_3CN, can produce metathesis reactions with dinuclear alkoxides such $W_2(OBu^t)_6$ to yield $(Bu^tO)_3W\equiv N$ and $(Bu^tO)_3W\equiv CMe$. In contrast $W_2[OCMe_2(CF_3)]_6$ reacts reversibly to give an adduct, $W_2[OCMe_2(CF_3)]_6(NCMe)_2.$[57]

Most alkoxides with simple groups are polymeric to the extent that maximum coordination of the metal is achieved. Some common types are shown in (11-XII) to (11-XIV) and the structure of another is illustrated in Fig. 11-3.
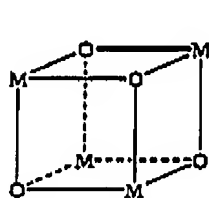
(Na OBu')₄
(11-XII)
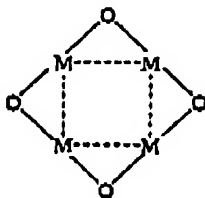
(CuOBu')₄
(11-XIII)
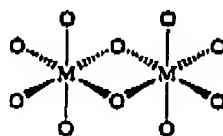
[Nb(OMe)₅]₂
(11-XIV)

The use of very bulky alkoxide or aryloxide groups such as $Bu^t_3CO^-$, $Bu^t_3SiO^-$, 2,6-di-t-butylphenoxide and adamantoxides can, however, give simple mononuclear species with low coordination numbers.

Alkoxo groups not engaged in bridging may, of course act as donors to other metal species. Thus $U(OPr^i)_6$ gives adducts with Li, Mg, and Al alkyls such as

[57]M. H. Chisholm, *J. Chem. Soc., Dalton Trans.* **1996**, 1781.

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(11-XV), while in the lithium salt of the $W(OPh)_6^-$ ion, two phenoxides are bound to Li^+ (11-XVI).
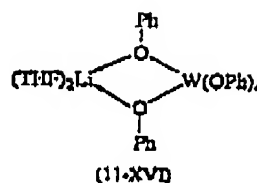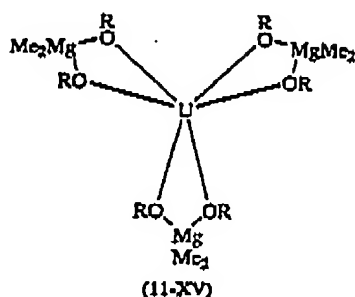
(11-XV)

(11-XVI)

Although aryloxides can form unidentate or bridge groups as in $W(OPh)_6$ and $(PhO)Cl_3Ti(\mu\text{-}OPh)_2TiCl_3(OPh)$, respectively, for Ru, Rh and Ir, the phenoxide ion can be bound as a η-1-5-oxocyclohexadienyl (11-XVII) where the C—O group becomes more keto-like and the bonding is delocalized.
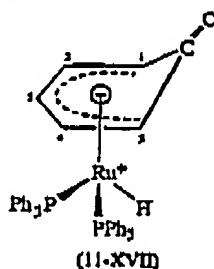
(11-XVII)

Chiral alkoxides[88] can be made using sugars, as in MoO_2L_2 and $MoO_2L_2(phen)$, where L is 11-XVIII.
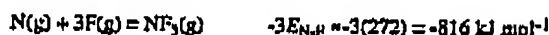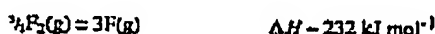

(11-XVIII)
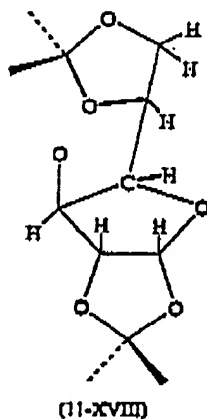
[88]C. Floriani *et al.*, *J. Chem. Soc., Dalton Trans.* 1995, 3329; *Prog. Inorg. Chem.* 1997, 45, 293; *Chem. Commun.* 1997, 183.

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molecular halides, such as those of B, C, Si, and P. Interhalogen compounds are discussed in the following sections.

Molecular Fluorides

Many molecular fluorides exist, but it is clear that because of the high electronegativity of fluorine, the bonds in such compounds tend to be very polar. Because of the low dissociation energy of F_2 and the relatively high energy of many bonds to F (e.g., C—F, 486; N—F, 272; P—F, 490 kJ mol^{-1}), molecular fluorides are often formed very exothermically; this is just the opposite of the situation with nitrogen, where the great strength of the bond in N_2 makes nitrogen compounds mostly endothermic. Interestingly, in what might be considered a direct confrontation between these two effects, the tendency of fluorine to form exothermic compounds wins. Thus for NF_3 we have
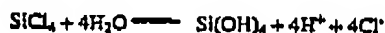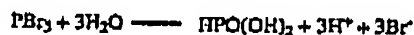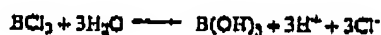
$$\tfrac{1}{2}N_2(g) = N(g) \qquad \Delta H - 475 \text{ kJ mol}^{-1}$$

$$\tfrac{3}{2}F_2(g) = 3F(g) \qquad \Delta H - 232 \text{ kJ mol}^{-1}$$

$$N(g) + 3F(g) = NF_3(g) \qquad -3E_{N-F} - 3(272) = -816 \text{ kJ mol}^{-1}$$

Therefore,

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}F_2(g) = NF_3(g) \qquad \Delta H = -109 \text{ kJ mol}^{-1}$$

The high electronegativity of fluorine often has a profound effect on the properties of molecules in which several F atoms occur. Representative are facts such as (a) CF_3CO_2H is a strong acid, (b) $(CF_3)_3N$ and NF_3 have no basicity, and (c) CF_3 derivatives in general are attacked much less readily by electrophilic reagents in anionic substitutions than are CH_3 compounds. The CF_3 group may be considered as a kind of large pseudohalogen with an electronegativity about comparable to that of Cl.

Reactivity

The detailed properties of a given molecular halide depend on the particular elements involved, and these are discussed where appropriate in other chapters. However, a fairly general property of molecular halides is their easy hydrolysis to produce the hydrohalic acid and an acid of the other element. Typical examples are

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3H^+ + 3Cl^-$$

$$PBr_3 + 3H_2O \longrightarrow HPO(OH)_2 + 3H^+ + 3Br^-$$

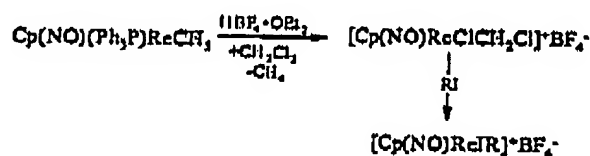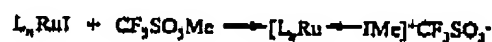$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4H^+ + 4Cl^-$$

When the central atom of a molecular halide has its maximum stable coordination number, as in CCl_4 or SF_6, the substance is usually quite unreactive toward water or even OH^-. This does not mean, however, that reaction is thermodynamically unfavorable, but only that it is kinetically inhibited, since there is no room for nucleophilic attack. Thus for CF_4 the equilibrium constant for the reaction

$$CF_4(g) + 2H_2O(l) = CO_2(g) + 4HF(g)$$
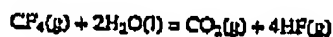
is $\sim 10^{21}$. The necessity for a means of attack is well illustrated by the failure of SF_6 to be hydrolyzed, whereas SeF_6 and TeF_6 are hydrolyzed at 25°C through expansion of the coordination sphere, which is not possible for sulfur.

Organic Halides as Ligands

There is an extensive chemistry of organic halides as ligands[20] that includes now R_3SiX.[21] The compounds can be obtained by reactions such as

$$L_nMCl + AgPF_6 + RI \xrightarrow[-AgCl]{CH_2Cl_2} [L_nM \leftarrow IR]^+PF_6^-$$

$$L_nRuI + CF_3SO_3Me \longrightarrow [L_nRu \leftarrow IMe]^+CF_3SO_3^-$$

$$Cp(NO)(Ph_3P)ReCH_3 \xrightarrow[\substack{+CH_2Cl_2 \\ -CH_4}]{HBF_4 \cdot OEt_2} [Cp(NO)ReClCH_2Cl]^+BF_4^-$$

$$\downarrow RI$$

$$[Cp(NO)ReIR]^+BF_4^-$$

Although the compounds are mainly of the angular type M···XR, there are numerous examples of compounds with bridging or chelate groups arising from halides such as CH_2I_2, $Cl(CH_2)_3Cl$, $I(CH_2)_3I$, and so on. An example is $[Ir^{III}H_2(PPh_3)_2(\eta^2\text{-}1,2\text{-}C_6H_4I_2)]^+SbF_6^-$. Silver complexes have been particularly well studied.[22] A different type of complex has an M···X—CH_2—M unit with an M—C bond;[23] aryl fluorides have also been shown to coordinate to $RuCl_2(PPh_3)_3$.[24] Compounds with organic halide ligands can be useful starting materials as the halides can often be easily replaced by other ligands.

[20]R. J. Kulawiec and R. H. Crabtree, Coord. Chem. Rev. 1990, 99, 89.
[21]R. U. Kirss, Inorg. Chem. 1992, 31, 3451.
[22]J. Powell et al., J. Chem. Soc., Dalton Trans. 1996, 1669; R. D. Gillard et al., Polyhedron 1996, 15, 2409.
[23]Y. Zhou and J. A. Gladysz, Organometallics 1993, 12, 1073.
[24]S. D. Perera and B. L. Shaw. Inorg. Chim. Acta 1995, 228, 127.